Highly site-specific H_2 adsorption on vicinal Si(001) surfaces

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Experimental and theoretical results for the dissociative adsorption of H_2 on vicinal Si(001) surfaces are presented. Using optical second-harmonic generation, sticking probabilities at the step sites are found to exceed those on the terraces by up to six orders of magnitude. Density functional theory calculations indicate the presence of direct adsorption pathways for monohydride formation but with a dramatically lowered barrier for step adsorption due to an efficient rehybridization of dangling orbitals.

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In most technological applications of surface chemistry, e.g. in catalysis, the surfaces used to promote a reaction are highly non-ideal. They contain steps and other imperfections in large concentrations, which are thought to provide reactive sites. Also in thin-film growth, steps are crucial for producing smooth layers via the so-called step-flow mode of growth. Despite the importance, detailed information about the role of steps is scarce. On metals, it is generally argued that the reactivity at steps is increased due to a lower coordination number of atoms [1]. On semiconductors, the situation is less clear since step and terrace atoms often attain similar coordination due to special reconstructions. The H_2/Si system provides a good model to study the role of steps, since it is the most thoroughly studied adsorption system on a semiconductor surface and it is of considerable technological relevance [2]. In addition, several recent studies came to conclude that the interaction of molecular hydrogen would be largely determined by defect sites [3,4], and in particular by steps [5,6].

In this Letter, we demonstrate that the contributions from terraces and steps to H_2 adsorption on vicinal Si(001) surfaces can be discriminated using the second harmonic generation (SHG) probe technique to monitor hydrogen coverages during gas exposure. The measured sticking coefficients differ by up to six orders of magnitude and indicate the presence of an efficient adsorption pathway at the steps, while adsorption on the terraces involves a large barrier. We performed density functional theory calculations to identify the relevant reaction mechanisms and to compare their energetics. Surprisingly, H_2 dissociation at the threefold-coordinated step atoms is found to proceed via two neighboring sites and directly leads to monohydride formation similar as at the dimerized terrace atoms. The huge differences in barrier heights arise from the interplay of lattice deformation and electronic structure effects. Thus, adsorption on a semiconductor surface may be highly site-specific, even if the reactive surface atoms have similar coordination.

The experiments were performed with Si samples that were inclined from the [001] surface normal towards the [110] direction by $2.5°$, $5.5°$ and $10° \pm 0.5°$. They were prepared by removing the oxide layer of the 10-Ωcm n-type wafers in ultra-high vacuum at 1250 K followed by slow cooling to below 600 K. Under these conditions double-atomic height steps prevail on the surface that have additional three-fold coordinated Si atoms attached to the step edges, the so-called rebonded D_B steps [7] (a stick-and-ball model is displayed in Fig. 1). Low energy electron diffraction (LEED) confirmed that the surfaces predominantly consisted of a regular array of double-height steps separated by terraces with a unique orientation of Si dimers. The sticking coefficients for the dissociative adsorption of H_2 on these surfaces were determined from the temporal evolution of the hydrogen coverage determined during gas exposure by SHG as described previously [8]. Accurate measurements of the H_2 desorption process [9] ensured that the recorded signal changes were not affected by small amounts of contaminants in the dosing gas which was purified in liquid nitrogen traps [8]. For the sensitive detection of step adsorption it was exploited that the presence of regular steps is associated with a symmetry break in the surface plane. For electric field components perpendicular to the step edges this en-
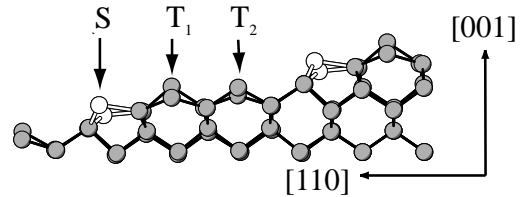

FIG. 1. Relaxed geometry for the rebonded D_B step of a Si(117) surface. The rebonded Si atoms are shown in white.
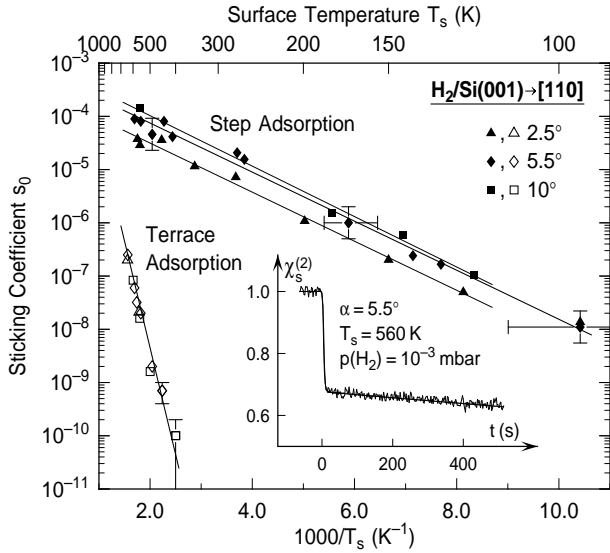
FIG. 2. Initial sticking coefficients s_0 for a gas of H_2 at room temperature on the steps (filled symbols) and terraces (open symbols) of vicinal Si(001) surfaces at various surface temperatures T_s. They were derived from the decay of the nonlinear susceptibility $\chi_s^{(2)}$ during H_2 exposure as shown in the inset. Numerical fits to an Arrhenius law $s_0(T_s) = A \exp(-E_a/kT_s)$ yield activation energies E_a and prefactors A for step (terrace) adsorption of 0.09 ± 0.01 eV (0.76 ± 0.05 eV) and $4 \pm 2 \times 10^{-4}$ ($\sim 10^{-1}$).

hances the SHG contribution of the step with respect to the terrace sites [10].

A representative measurement taken at the $5.5°$ sample, kept at a temperature of 560 K and exposed to H_2 at a pressure of 10^{-3} mbar is displayed in the inset of Fig. 2. There is a rapid drop of the surface nonlinear susceptibility $\chi_s^{(2)}$ responsible for the SHG signal immediately after admitting H_2 gas to the chamber followed by a more gradual decay. The two slopes of the $\chi_s^{(2)}$ correspond to sticking probabilities of 1×10^{-4} and 1.4×10^{-8}. The initial sticking coefficients s_0 measured for the different samples at various temperatures are collected in the form of two Arrhenius plots in the main part of Fig. 2. They span a very wide range from 10^{-10} up to 10^{-4} [11].

We attribute the fast hydrogen uptake – which is not present on the Si(001) surfaces – to adsorption at special dissociation sites of the stepped surface and identify the slow signal decay with adsorption on terrace sites. This interpretation is corroborated by the good agreement between the absolute values of the smaller sticking coefficients with those obtained previously for nominally flat Si(001) [8] and by the correlation of the saturation coverage θ_{step}^{sat} associated with the fast decay with the miscut angle (Table I). θ_{step}^{sat} was determined by means of temperature programmed desorption (TPD) after saturation was detected by SHG. With the exception of the

α	R_{db}	θ_{step}^{sat}
$2.5°$	0.064	0.07
$5.5°$	0.146	0.12
$10°$	0.285	0.15

TABLE I. Ratio R_{db} of dangling bonds at rebonded D_B steps to total number of dangling bonds on vicinal Si(001) surfaces with miscut angle α towards [110] and measured saturation coverage of hydrogen at the steps θ_{step}^{sat}.

$10°$ sample – where the number of D_B steps might be reduced as a result of facetting [12] – θ_{step}^{sat} is found to be in good agreement with the fraction of Si dangling bonds located at the steps relative to the total amount of dangling bonds in a unit cell of the vicinal surface R_{db} (Table I). Thus it is tempting to associate the hydrogen species adsorbed at the steps with monohydrides formed by attaching hydrogen to the rebonded Si atoms.

For a quantitative comparison of the measured sticking coefficients for step and terrace adsorption it is important to know whether they are due to independent processes. Annealing and readsorption experiments show that surface temperatures in excess of 600 K are required to cause appreciable depletion of the step sites by hydrogen migration on a timescale of several hundred seconds [10]. For this reason it can be excluded that hydrogen adsorption on terraces is mediated by the step sites under the conditions of our experiments. The two sticking coefficients given in Fig. 2 are thus a quantitative measure of the reactivity of different surface sites. The strongly activated behavior observed for terrace adsorption, characterized by an Arrhenius energy of $E_a = 0.76$ eV, is similar to that reported previously for the well oriented Si(001) and Si(111) surfaces. It indicates that distortions of the lattice structure have a pronounced effect in promoting dissociative adsorption of H_2 [13]. With $E_a = 0.09$ eV the effect of temperature on step adsorption is comparatively moderate.

The experimental data suggest that the peculiar geometric and electronic structure of the stepped surface gives rise to reaction channels that are much more effective than those on ideal surfaces. To gain an atomistic understanding of the underlying mechanisms we determined the total energy of various atomic configurations from electronic structure calculations. We use density functional theory with a plane-wave basis set [14]. The exchange-correlation functional is treated by the generalized-gradient approximation (GGA) [15]. For silicon we generate an *ab initio*, norm-conserving pseudopotential [16], while the bare Coulomb potential is used for hydrogen. We perform a transition state search for H_2 dissociation in the configuration space of the H atoms and the Si atoms of the four topmost layers using the ridge method [17]. All calculations, including geometry optimizations, are performed with plane waves up to a

cut-off energy of 30 Ry in the basis set. For the barrier heights reported below, the calculations are repeated with the same geometries, but with a cut-off of 50 Ry. We model the D_B step by a vicinal surface with Miller indices (1 1 7), using a monoclinic supercell. In this geometry, periodically repeated rebonded D_B steps are separated by terraces two Si dimers wide. Two special **k**-points in the irreducible part of the Brillouin zone are used for **k**-space integration. The uncertainty in chemisorption energies due to the finite cell size is determined to be less than 30 meV.

The optimized geometry for the rebonded D_B step is shown in Fig. 1. The rebonded Si atoms form unusually long bonds to the atoms at the step edge (mean bond strain 6%). Furthermore, the height of the rebonded Si atoms at the step edge is different by 0.67Å, due to a Jahn-Teller like distortion similar in physical origin to the buckling of the Si dimers on the Si(001) surface. Consequently, the surface is semiconducting with a Kohn-Sham gap of ~ 0.5eV.

We investigated the following mechanisms of H_2 dissociation close to a D_B step: i) Si dimers at the end of a terrace could have different reactivity compared to the Si dimers on flat regions of the surface. ii) The H_2 breaks the stretched bond of a rebonded Si atom forming a dihydride species. iii) The H_2 molecule approaches with orientation parallel to the step and dissociates, each of the H atoms attaching to one of the Si rebonded atoms.

To determine the importance of mechanism i), we locate the transition states both for H_2 dissociation on the terrace Si dimer directly above and below the step (T_1 and T_2 in Fig. 1). The geometries of these transition states are asymmetric, with the H_2 molecule dissociating above the lower atom of the Si dimer, similar to the transition state found for the ideal Si(001) surface [18]. For the barrier heights we obtain 0.40 eV and 0.54 eV for the sites T_1 and T_2, respectively. These results are close to the adsorption barrier of 0.4 eV determined previously for the flat Si(001) surface using the same exchange-correlation functional [19]. Hence, the Si dimers near steps are only slightly different in reactivity from Si dimers on an ideal Si(001) surface. Thus mechanism i) cannot explain the enhanced reactivity.

Mechanism ii), the formation of a dihydride at the step from a gas phase H_2 molecule and a rebonded Si atom, is considerably less exothermic (0.9 eV) than monohydride formation (~ 2 eV), because the Si–Si bond between the rebonded Si atom and the step must be broken. Nevertheless, dihydrides would exist as metastable species at the surface temperatures of the experiment provided the corresponding adsorpion barrier were sufficiently low. However, the calculations yield a barrier of 0.50 eV, even slightly higher than the one for monohydride formation on the terraces, and we rule out mechanism ii) as well.

For mechanism iii), monohydride formation from a molecule approaching parallel to the step, we do not find
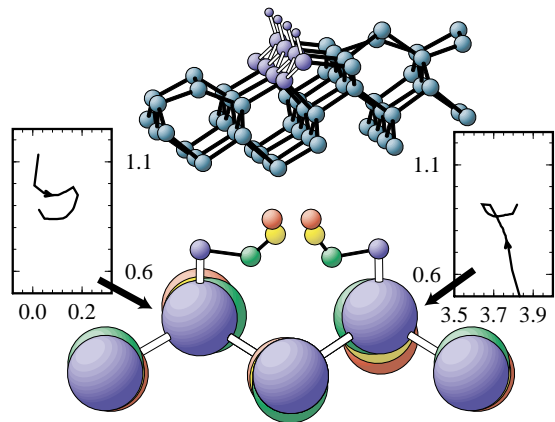

FIG. 3. Monohydride at the step (upper part) and and motion of the highlighted step atoms during H_2 dissociation (lower part). The reaction path is projected onto a (110) plane parallel to the D_B step with different stages of dissociation marked by different colors. The insets show the motion of the rebonded Si atoms (coordinates in Å).

any barrier. Using damped *ab initio* molecular dynamics for a slowly approaching molecule, we can identify the reaction path connecting the gas phase continuously with the monohydride at the step. Hence we attribute the highly increased sticking coefficient of H_2 observed on the vicinal surfaces to direct monohydride formation. This conclusion is confirmed by the observation that this mechanism is compatible with the observed saturation coverages of Tab. I, as opposed to a complete decoration of the step with dihydride species, which would result in a saturation coverage a factor of two higher than observed. Tab. II summarizes the energetics of the three reaction mechanisms considered.

Fig. 3 illustrates the concerted motion of the H atoms and the two rebonded Si atoms along the reaction path. The Jahn-Teller like splitting showing up in the different height of the two rebonded Si atoms is undone during the approach of the H_2 molecule. Additionally, the two rebonded Si atoms move closer together by about 0.4Å during adsorption to assist in breaking the H–H bond. Both for this optimum pathway and for the similar, but slightly less favorable, pathway with the adsorption site

site	E_{ads}[eV]	E_{chem}[eV]
S (monohydride)	no barrier	−2.07
S (dihydride)	0.50	−0.87
T_1	0.40	−1.75
T_2	0.54	−1.93

TABLE II. Adsorption barriers E_{ads} and chemisorption energies E_{chem} for H_2 molecules reacting with the vicinal surface at the sites S, T_1 and T_2, as indicated in Fig. 1.
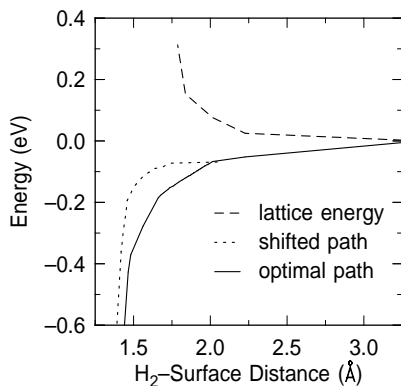
FIG. 4. Total energy of the H_2/surface system along the adsorption path shown in Fig. 3 (full line). The dashed line comes from a separate calculation for the bare Si surface using the Si coordinates along the reaction path. The thin dotted line denotes the total energy along a similar reaction path, with the two H-adsorption sites translated by one surface lattice constant along the step edge.

shifted by one surface lattice constant parallel to the step, the total energy decreases monotonically when the H_2 molecule approaches the surface (Fig. 4, full and dotted lines). This is to be compared to the adsorption energy barrier of 0.3 eV we have calculated for a rigid Si substrate. Obviously, a particular distortion of the step Si atoms is crucial for adsorption, which, on the bare surface, would be associated with a sizeable elastic energy (dashed curve in Fig. 4). Together with the small density of step sites (cf. R_{db} in Tab. I) and the necessary alignment of the H_2 axis parallel to the step, this explains the small prefactor A_{step} in comparison to $A_{terrace}$. The reaction path shown in Fig. 3 implies some transfer of energy and momentum from the H_2 to the lattice during the adsorption process, which is not easily achieved due to the large mass mismatch. However, thermal fluctuations will sometimes lead to lattice configurations favorable for adsorption. Therefore, the surface temperature dependence of sticking, as suggested by the experiments, appears to be compatible with the presence of a non-activated adiabatic pathway.

We find that atomic relaxation close to a step, while inducing only moderate changes in the chemisorption energy [20], has a pronounced influence on the energetics of adsorption. Since the early stages of H_2 dissociation are quite sensitive to electronic states around the Fermi energy, we propose that the increase in reactivity is due to shifts of electronic states in the gap induced by lattice distortions. In the surface ground state, the two surface bands formed from the dangling orbitals located at the rebonded Si atoms bracket the Fermi energy and are split by ~ 1 eV due to the Jahn-Teller mechanism. However, when the two rebonded Si atoms are forced to

the same geometric height, the energy separation of the centers of the surface bands is reduced to 0.4 eV. Upon the approach of molecular hydrogen, these surface states can rehybridize and thus interact efficiently with the H_2 molecular orbitals. The electronic structure at the step is different from the surface band structure of the ideal Si(001) dimer reconstruction: At the Si dimers characteristic for the ideal surface, the π-interaction of the dangling bonds prevents the two band centers to come closer than 0.7eV [21], while the dangling bonds of equivalent step edge Si atoms are almost degenerate. Therefore the terrace sites are less capable of dissociating a H_2 molecule than the step sites.

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